Monitoring of Arsenic Occurrence in Intertidal Sediments of River Scheldt (Belgium)

S. K. Chapagain [1], G. Du Laing [2], M. Verloo [2], S. Shrestha [1] and F. Kazama [1]
[1] Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11, Takeda, Kofu, Yamanashi, 400-8511, Japan

[2] Laboratory of Analytical Chemistry and Applied Ecochemistry, Faculty of Bioscience Engineering,
Ghent University, Coupure Links 653, Gent -9000, Belgium

Corresponding Author: S. K. Chapagain (saroj@yamanashi.ac.jp)

ABSTRACT

This study aims to assess the occurrence of arsenic in the intertidal sediments of River Scheldt in Belgium. Samples of the sediments were collected from eleven different locations along the River Scheldt up to 100 cm depth and analysed for physicochemical properties including arsenic contents. The study revealed that the arsenic contents in the sediment samples varied in a wide range, from 2.3 to 140.2 mg kg^{-1} dry weight. However, the arsenic concentrations were generally below the background concentrations and the remediation thresholds of arsenic in Flanders, Belgium. In addition, it is observed that a strong positive correlation exists between arsenic, organic matter and clay contents. On the contrary, negative correlation exists between arsenic, sand and pH. Based on the regression studies between organic matter and arsenic, it is recommended that proper management practices has to be developed that stops the increase in organic matter in the study areas.

Keywords: Arsenic, sediments, Scheldt River, Belgium

1. INTRODUCTION

The River Scheldt is a lowland river, which originates from the northern part of France and flows into the North Sea in the Netherlands. The River Scheldt is subject to tidal fluctuation in the estuarine part which extends from the mouth to the city of Ghent, about 160 kilometres inland. In the estuarine part of the basin, the intertidal areas are valuable, natural areas as it involves fresh, brackish and saltwater marshes. Andreae and Andreae (1989) have reported arsenic (As) pollution in the River Scheldt, ascribing this to the watershed being a densely populated and industrialized region in central Europe. The Zenne River, a tributary which flows through the centre of the Brussels industrial region, was found to supply most arsenic in the River Scheldt.

It has been accepted that arsenic contamination in the environment is causing a significant global health problem, a wide variety of adverse health effects have been attributed to chronic exposure to high level of arsenic (Ng et al., 2003). Many studies concerning other pollutants have been conducted with respect to the River Scheldt. However, only limited studies have been carried out to explore the occurrence and distribution of arsenic in riparian areas of River Scheldt. Moreover,

the fate of arsenic has not yet been studied in the intertidal river sediments. Hence, a study was carried out primarily to assess the distribution of arsenic within the intertidal sediments of River Scheldt and to explore the arsenic retention relationship with some important physicochemical sediment properties.

2. MATERIALS AND METHODS

The sediment samples were collected from eleven locations (thirteen different sites) along the River Scheldt in the provinces of Antwerp and the East of Flanders, Belgium (Figure 1). The samples were collected from different depths of sediments: 0-20 cm, 20-40 cm, 40-70 cm, 70-100 cm. However, these samples are referred as depths of 10 cm, 30 cm, 60 cm and 90 cm in the subsequent text. During sampling, sediment samples from each site were collected from three sampling points which were selected randomly apart from each site by considering the heterogeneity. Similarly, three sampling sites were selected within 10 meter apart rather than randomly in Doel to capture the spatial variability in the arsenic distribution.

Figure 1. Sampling locations along the River Scheldt

The samples were packed separately, labelled properly and transported to the laboratory in plastic bag. Part of the sample was air dried and subsequently grinded to a diameter smaller than 2 mm. The grinded samples were used for the most of the analyse; analysis for texture was performed by using laser diffraction (Coulter LS200, Miami, FL) after removing organic matter and carbonates by adding hydrogen peroxide and an acetate buffer solution respectively. pH was determined by 1:5 sediment-distilled water suspension after equilibration of 18 h (Van Ranst et al., 1999); Calcium carbonate ($CaCO_3$) content was determined by back-titration with 0.5 M NaOH of an excess of H_2SO_4 added to 1 g of air-dried sediment (Van Ranst et al., 1999). Similarly, chloride content was determined as potentiometric titration with $AgNO_3$ (Van Ranst et al., 1999). Organic matter (OM) was analysed by the weight loss method after 2 h at 450°C temperature treatment (Loss On Ignition, LOI), Likewise, cation exchange capacity (CEC) is determined by saturating of the adsorption complex by the ammonium ion (NH_4^+) and subsequently quantitative analysis of ammonium after desorption by K^+. Acid volatile sulphur (AVS) was determined by volatilization of sulfides after addition of 12 M HCl to the sediment. The evolved H_2S was trapped in a Zn-acetate solution, and determined by iodometric titration (Tack et al., 1997a). The analyses of AVS contents were performed directly on fresh sediment samples. Extraction of the arsenic from

the sediments was obtained by digesting them in mixture of concentrated acids, and the subsequent analysis of arsenic was performed using hydride generation Atomic Absorption Spectrometry (AAS, Varian, Palo Alto, CA) with following the standard procedure *(Laboratory of Analytical Chemistry and Applied Ecochemistry, Ghent University, Belgium)*. Texture, CEC and AVS contents were determined by mixing equal proportions of sample from the three sampling points at each sampling location and depth, where as rest of the parameters were analyzed separately.

3. RESULTS AND DISCUSSION

The analytical results of the sediment samples are presented below in Table 1. The result reveals parameters are quite variable with high range. However, average pH value of the sediments was found at neutral with the minimum and maximum value; 7.36 and 8.16 respectively. Furthermore; slightly higher average value of pH was observed at upper layer of the sediment which is thought due to the increased root activities and decomposing of the organic matter. The content of the organic matter was higher in the sediment samples. It was observed that the organic matter content was higher at upper layer which was slightly decreases with the depth. The higher level of organic matter might be the result of the abundance of riparian vegetation.

Table 1. The physicochemical properties of the sampled sediments at different depths

Depth	**pH**	**EC** (μscm^{-1})	**Chloride** ($g\ Cl^{-}kg^{-1}DM$)	**OM** (%)	**$CaCO_3$** (%)	**Clay** (%)	**AVS** ($mg\ kg^{-1}$ DM)
10 cm							
Avg	7.58	1733	1.63	9.03	14.0	40.3	32
St dev	0.16	1410	1.63	4.35	5.53	10.9	41
Med	7.56	1108	0.97	7.87	14.9	40.9	13
Min	7.36	292	0.02	2.5	4.67	22.8	2
Max	7.89	4810	4.75	17.7	25.4	53.9	127
30 cm							
Avg	7.74	1623	1.61	7.05	11.5	35.0	46
St dev	0.25	1338	1.85	3.42	6.23	15.3	43
Med	7.77	1263	0.64	6.66	11.1	38.8	33
Min	7.36	209	0.001	1.82	2.96	13.6	<2
Max	8.16	5077	6.19	12.4	22.5	58.2	132
60 cm							
Avg	7.76	1698	1.54	7.58	11.5	38.6	103
St dev	0.23	1180	1.68	2.7	5.71	14.4	110
Med	7.76	1346	0.59	8.15	11.4	42.9	65
Min	7.43	269	0.02	2.15	2.4	11.5	<2
Max	8.08	4140	4.94	12	20.8	58.9	402
90 cm							
Avg	7.78	1790	1.54	8.99	10.4	38.7	144
St dev	0.22	1260	1.71	3.65	4.15	13.3	142
Med	7.87	1133	0.28	9.67	10.8	44.8	99
Min	7.43	299	0.001	2.73	2.21	12.3	3
Max	8.09	3903	5.01	15.0	15.2	54.5	533

(Avg: Average, St dev: Standard deviation, Med: Median, Min: Minimum, Max: Maximum)

The observed variation with electrical conductivity (EC) and chloride contents (Table 1) can be explained due to differences in the distance of the sampling locations from the river mouth. The chloride content was found decreasing with the increasing distance from the river mouth. A wide range of AVS value (<2-533 mg kg^{-1} DM) suggests the locations are varying with redox condition. Furthermore, AVS was increased with the depth indicating increase in reducing condition with increase in depth. The maximum percentage (58.9%) of clay was found at 60 cm depth where as average clay percentage was higher at upper 10 cm depth. The maximum amount of calcium carbonate was occurred at 10 cm depth.

3.1 Arsenic Content in the Sediments

The arsenic content ranged from 2.3 mg kg^{-1} to 140.2 mg kg^{-1} of dry weight (Figure 2). The maximum (140.2 mg kg^{-1}) arsenic content was observed in the sediments of Galgenweel followed by Kijkverdriet and Bornem. Rupelmonde and Bazel sites had lower (2.3 mg kg^{-1}) arsenic contents.

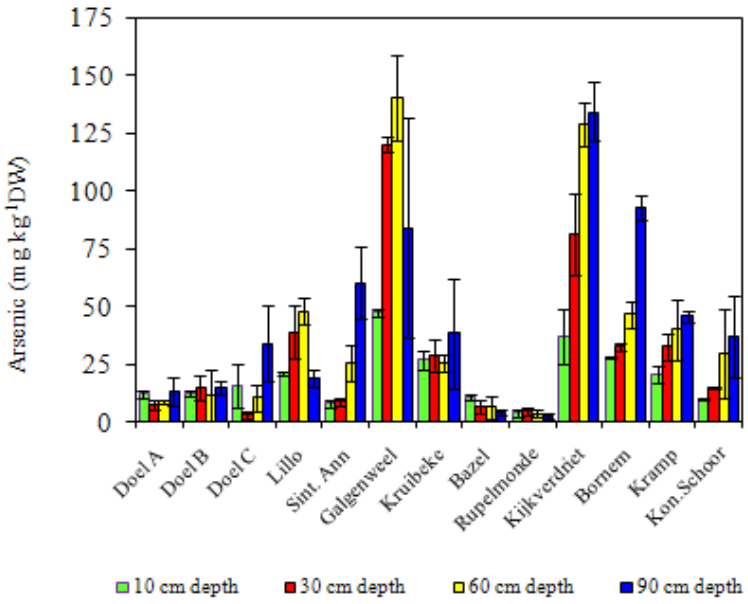

Figure 2. Arsenic concentration in different depths of sampled locations of River Scheldt

Furthermore, the relationship between the arsenic content with sediments was assessed based on correlation analysis among arsenic and some major physicochemical properties of the sediment (Table 2). The amounts of arsenic contents were positively correlated with organic matter and clay contents and negatively with sand content and pH.

Table 2. Correlation coefficient of arsenic contents in the intertidal sediments with clay, sand, organic matter, pH, and CEC

Depth	Correlation	r value
10 cm	As x % Clay	0.647
	As x % Sand	-0.320
	As x % Organic matter	0.846
	As x pH	-0.519
	As x CEC	0.803
30 cm	As x % Clay	0.673
	As x % Sand	-0.600
	As x % Organic matter	0.786
	As x pH	-0.650
	As x CEC	0.787
60 cm	As x % Clay	0.662
	As x % Sand	-0.546
	As x % Organic matter	0.822
	As x pH	-0.620
	As x CEC	0.843
90 cm	As x % Clay	0.645
	As x % Sand	-0.650
	As x % Organic matter	0.701
	As x pH	-0.651
	As x CEC	0.669

(Monitoring location = 11, replication = 3, each depth's value was average of 3 samples)

The arsenic retentive capacity of sediments was influenced by its physicochemical properties. The influence of organic matter on heavy metals sorption is widely reported, however its role on arsenic sorption has not been well demonstrated. Some recent study has suggested the amount of arsenic content in soil associated with organic matter. The occurrence of higher arsenic concentrations with increasing organic matter content is explained possibly due to the formation of organo-arsenic complexes by arsenic in association with the aromatic as well as the hydrogenetic fraction of organic matter (Paikaray et al., 2005). The positive correlation between the arsenic and organic matter content was also observed in soil at Habiganj district in Bangladesh (Hossain, et al., 2001). In other hand, the higher specific surface area of the clay minerals might be an important factor in the adsorption of arsenic. In addition, the arsenic retention depends on the quantity and type of clay. Corwin et al.'s study has supported our findings of positive correlation between arsenic and clay contents. In general, soils with higher clay contents retain more arsenic than soils with lower clay content (Corwin et al., 1999). On the contrary, arsenic has a shorter residence time in sandy soils, especially under alkaline conditions (Hartley et. al., 2004), which has further supported our finding on negative correlation between arsenic and the sand content.

Oxides of iron, aluminum and manganese are considered as potentially the most important source/sinks for arsenic in the sediments because of their chemistry, wide spread occurrence, and tendency to coat other particles. The influence of pH upon sorption depends upon sorbent material and chemical form of As. Adsorption affinity is reported higher for As (+V) at lower pH values and for As (+III) at higher pH values (Stollenwerk et al., 2003). However, analysis of total arsenic content was made, while the content of different arsenic species was not quantified. The results revealed the arsenic retentive capacity may decrease with increase in pH.

3.2 Correlation of Arsenic Distribution with Depth

The arsenic content was weakly correlated to the depth of sediments. In other hand, strong relationships were observed with the arsenic and sediments major physicochemical properties. Those relationships have been supposed to have direct impact on arsenic distribution rather than the depth itself.

3.3 Evaluation of Arsenic with Guideline

The occurrence of arsenic was evaluated with reference to the Flemish Decree on Soil Sanitation (VLAREBO, 1996). The background concentration levels for the Flemish soils are defined as; these concentrations commonly found in soils that are considered clean, and are function of soil organic matter and clay content (Tack et al., 1997b). Sanitation thresholds for different land use classes in the Flemish regulations indicate threshold levels for both the solid part of the soil and groundwater above which action must be taken to remediate the soil.

Table 3. The background and remediation level of Arsenic (As) (VLAREBO, 1996)

Location	Background level of As ($mg\ kg^{-1}$)	Remediation level of As ($mg\ kg^{-1}$)	*Avg As concentration ($mg\ kg^{-1}$)	*Avg clay (%)
Doel A	26.28	62.23	10.52	24.55
Doel B	28.59	67.71	13.61	29.18
Doel C	30.13	71.35	15.75	32.25
Lillo	34.85	82.54	31.65	41.70
St.Annastrand	29.38	69.57	25.8	30.75
Galgenweel	38.33	90.77	97.84	48.65
Kruibeke	38.34	90.80	29.85	48.68
Bazel	26.21	62.08	7.06	24.43
Rupelmonde	22.70	53.76	3.66	17.40
Kijkverdriet	41.20	97.58	95.40	54.40
Bornem	38.56	91.33	50.03	49.13
Kramp	36.85	87.28	34.68	45.70
Konkelschoor	38.65	91.54	23.00	49.30

(*Avg: Average)

While comparing the average concentration of arsenic with the background and remediation value, the arsenic status in the sediments along the River Scheldt are generally below the background and the remediation threshold level. However, sample from only one site (Galgenweel) has slightly exceeded the remediation threshold level.

3.4 Relationship between Arsenic and Organic Matter Content

In general, texture and pH are considered more stable parameters than organic matter of the sediments. The content of organic matter may change with time which may influence in the arsenic retention with sediments. Therefore, regression analysis was performed between arsenic and organic matter content (Figure 3). This relationship is important for predicting the changes in arsenic with respect to the changes in organic matter content. The abundance of riparian vegetation along the River Scheldt, may influence in the organic matter contents of the sediment with time and the situation may lead to possible redistribution of arsenic within the sediment layer.

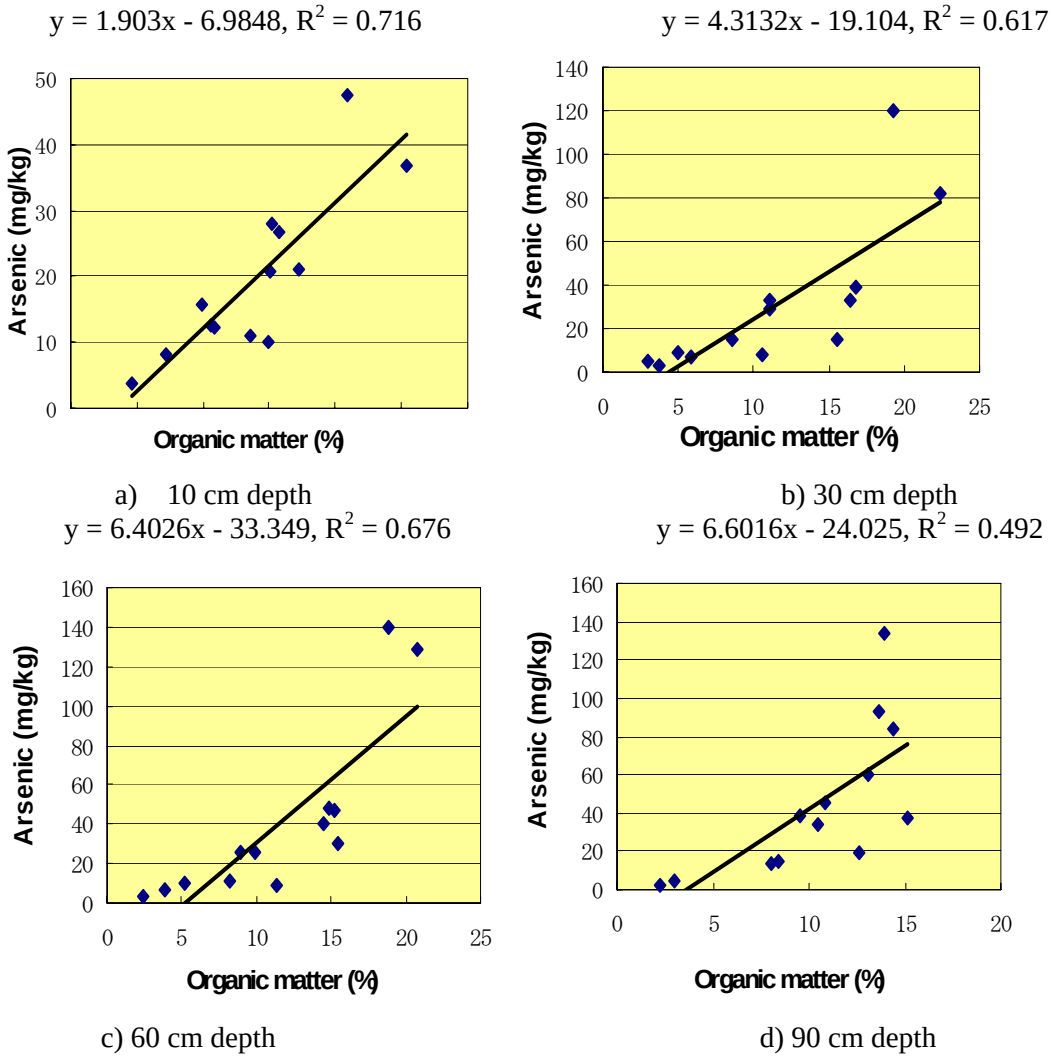

Figure 3. Regression relationship between organic matter and arsenic with depths

4. CONCLUSIONS

The following conclusions can be drawn from the study;

- The arsenic contents in the sediments along the River Scheldt were generally below the background levels and the remediation thresholds of arsenic in Flemish soils.
- The distribution of arsenic within sediment samples were related to the sediments physicochemical properties. Arsenic contents showed positive correlation with the organic matter and clay contents, a negative correlation with sand content and pH.
- Management practices affecting organic matter content may reduce the arsenic content with the sediments.

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